RAMAN AND ELECTROCHEMICAL NOISE SENSORS FOR IN-TANK CORROSION MONITORING

TECHNOLOGY DESCRIPTION

The proposed technology will use an echelle-based Raman spectrograph with a fiber-optic Raman sensor that can be deployed *in situ* in waste tanks. The instrument can detect nitrate, nitrite, and hydroxide over the full range of concentrations of significance to U.S. Department of Energy (DOE). The instrument will be operated remotely with only a small, lightweight probe and fiber-optic cable deployed in the tank. The Raman sensor will be housed in a compact sampling chamber with a filtering mechanism to allow only liquid waste to enter the sampling area. A remotely operated deployment platform that interfaces with the riser opening in the waste tank will be used to deploy the Raman probe into the waste. This is done via a pulley mechanism inside the platform. The deployment platform is completely sealed to protect workers from being exposed to the radiation plume emanating from the riser opening.

Using a Raman sensor for in-tank monitoring has several advantages that make it the technique of choice for monitoring anionic species such as nitrate, nitrite, and hydroxide. First, the Raman spectrum is unique for every molecule and can therefore be used as a “chemical fingerprint” to identify unknown species. The Raman technique can also differentiate between solid and dissolved species, which is important in waste tanks where the physical composition can range from liquid to sludge to hard saltcake. Another advantage of the Raman technique is ease of sampling. Furthermore, use of the Raman technique requires no sample preparation, so samples can be easily analyzed *in situ* if a fiber-optic probe is used to deliver and collect the scattered light from the sample.

An electrochemical noise (EN) sensor developed at Hanford and the Savannah River Site (SRS) is being co-deployed with the Raman sensor. The two sensors are being integrated into a single probe head. The EN technique has the capability of monitoring both localized and general corrosion. Localized corrosion including pitting and stress corrosion cracking is of concern in the waste tanks. EN measures the potential and current fluctuations of metal in solution. These fluctuations are perturbations resulting from the electrochemical reactions occurring at the metal surface and are low-frequency (1 Hz), small amplitude signals.

TECHNOLOGY NEED

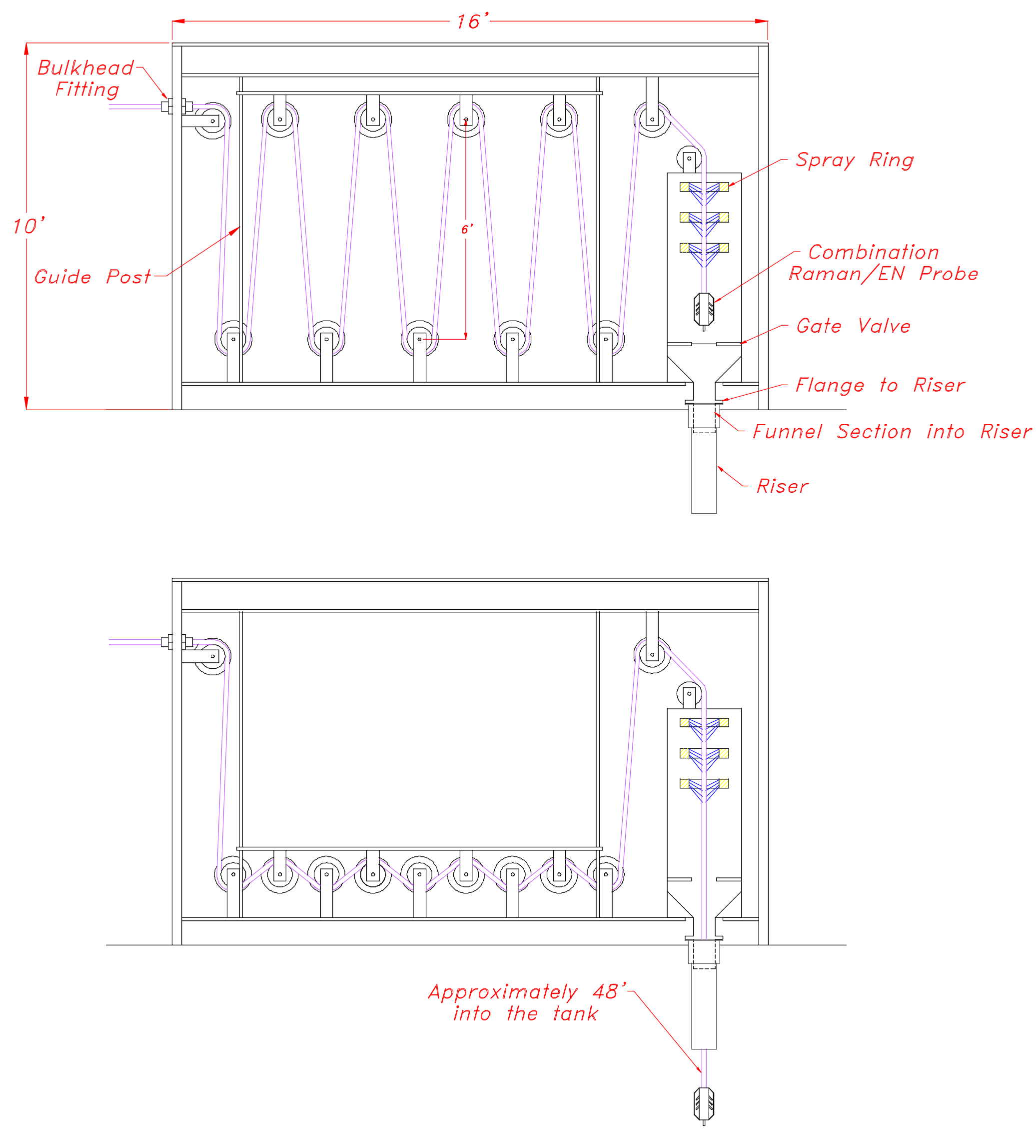
The DOE has 332 underground tanks used to process and store more than 100 million gallons of high-level, radioactive chemical waste. Some of the tanks have up to a one-million-gallon capacity, and many are of single-shell, steel construction. These tanks pose a considerable risk to the public and the environment should corrosion or other processes compromise the tank walls. Corrosion is of particular concern because many of the tanks contain high concentrations of nitrate, which attacks steel. Nitrate is a product of nuclear weapons materials processing. To minimize the effects of nitrate, the tank contents are maintained at an elevated pH (through the addition of sodium hydroxide) and are also maintained at an optimum nitrite level.

To ensure that the chemistry in a waste tank is being maintained to minimize corrosion, it is important to periodically monitor the concentrations of nitrate, nitrite, and hydroxide (NO3-, NO2-, and OH-). If significant changes in the concentrations are observed, then appropriate measures can be exercised to restore optimum, anti-corrosive conditions. Current analytical protocols for the analysis of NO3-, NO2-, and OH- in high-level waste tanks involve liquid sampling, preservation, transport, storage, preparation, and analysis with a pH meter and an ion chromatograph in a hot cell. These steps are slow, expensive, and present a major risk for site personnel and analysts. High costs serve to limit the number of samples collected from any one tank. There is also considerable opportunity for the sample composition to change or become contaminated from the time it is collected to when it is prepared for analysis.

An attractive alternative to existing protocols is to use one or more sensors to monitor *in situ* the three oxyanion species of interest. Small inexpensive devices that can be sacrificed, if necessary, are most appealing. Optical techniques employing fiber-optic probes are promising for this application because, unlike electrical devices, they are affected less by radiation. The important challenge for *in situ* fiber-optic sensors is for them to provide analytical data at relevant concentrations under harsh conditions such as those encountered in a waste tank. Waste tank probes will be exposed to 1,000 rad/hr, 90 °C, and 10 molar OH-. Furthermore, the measurements of the specified analytes must be performed in turbid solutions without interference from other sample components.

The need identified by the Site Technology Coordination Group (STCG) is as follows:

SR99-2045 – *In Situ* Waste Tank Corrosion Probe



Deployment Platform for the Combined Raman/Electrochemical Noise Sensor for In-Tank Corrosion Monitoring

TECHNOLOGY BENEFITS

Implementing the proposed combined *in situ* Raman and EN sensors will significantly reduce analysis time (including sample holding time, which normally can be weeks or more), cost (by eliminating all the steps prior to analysis as well as the need for specialized facilities and equipment for the analysis), and risk to site workers (“hot” samples do not have to be handled or transported). We estimate conservatively that the cost per sample will be reduced to about 10% of current levels based on the procedures and equipment/facilities that are eliminated from the standard protocols. The faster, less expensive *in situ* approach will allow more samples to be analyzed in each tank, providing more reliable characterization of the contents.

The incorporation of the electrochemical noise sensor will also provide a means to determine the type of corrosion processes occurring at the tank wall and cooling coils. Integration of the Raman and EN sensors into one probe will have the added advantage that real-time correlation between inhibitor concentrations and corrosion rates can be determined in an actual radioactive waste tank environment.

TECHNOLOGY CAPABILITIES/LIMITATIONS

The combined Raman/EN sensors will provide an *in situ* real time quantification of NO3-, NO2-, and OH- and a means to determine the type of corrosion processes at tank wall and cooling coils in underground storage tanks. The Raman sensor can also monitor other oxyanions (e.g., ferrocyanide/ferricyanide) or organic chemicals such as chlorinated hydrocarbon solvents in tanks. The Raman sensor can also be used to analyze the contents of 55-gallon drums, bottles, and other waste containers slated for disposal by incineration or other means. Operation of the combined Raman/EN sensor will require a skilled technician.

COLLABORATION/TECHNOLOGY TRANSFER

EIC Laboratories, Inc. (EIC) has developed a small fiber-optic Raman probe under DOE programs sponsored by Argonne National Laboratory and the Federal Energy Technology Center. The Raman probe has been awarded a U.S. Patent (No. 5112127). EIC has also developed an echelle-based Raman spectrograph under a DOE program also sponsored by the Federal Energy Technology Center. This Raman spectrograph is compact and field deployable, has no moving parts, and allows the acquisition of the entire Raman spectrum (“fingerprint” to OH^- regions). These DOE-developed sensor and instruments will be used in this program. The incorporation of the electrochemical noise sensor into the Raman probe is done in collaboration with Savannah River Technology Center. The deployment of the Raman system into tanks will be a joint venture between EIC and SRS personnel.

ACCOMPLISHMENTS AND ONGOING WORK

The feasibility of quantifying nitrates, nitrites, and hydroxide using the Raman technique has been demonstrated. All necessary steps have been taken to justify and safely deploy an *in situ* probe in high-level waste tanks. This technology provides costs savings and reduces employee exposure risks.

- Materials that will be used in the construction of the probe have been tested under tank conditions such as maximum radiation exposure (1,000 rad/hr exposure for two years), high pH, and 90 °C temperature. The probe materials have been demonstrated to survive waste tank conditions.
- The fabrication of the echelle-based spectrograph that will be used with the Raman probe has been completed.
- The conceptual design and requirements of the combined Raman/EN probe and sampling chamber that will be deployed into the tank have been established.
- The design for the deployment platform that will be used for deploying the probe into tank has been completed. The deployment platform uses a pulley mechanism for deploying the probe.
- An initial function and requirement document has been submitted and has undergone safety review at the SRS.

The remaining tasks for FY 1999 will be the start of “hot” cell testing at the SRS and the fabrication and cold acceptance test of the combined Raman/EN sensor and deployment platform.

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